Molecular Astrophysics: Study of Interstellar Cyanopolyynes

Final Report

Science Academies'

Summer Research Fellowship

by

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Under Supervision

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1 April – 30 May, 2016

Certificate

This is to certify that **Mr. Bhaskar Anand** (Summer Research Fellow 2016, Registration No.-PHYS80) worked under my supervision for 8 weeks, during 1April – 30 May, 2016. He is submitting herewith this report entitled "*Molecular Astrophysics: Study of Interstellar Cyanopolyynes*" based on the work carried out by him during this period. The work was carried out using the facilities available in our laboratory at the Department of Physics, DDU Gorakhpur University, Gorakhpur.

(Shantanu Rastogi)
Professor,
Department of Physics,
DDU Gorakhpur University,
Gorakhpur – 273 009

Place: Gorakhpur
Date: 30.05.2016

Acknowledgment

It is a pleasure for me to present this Final Report. I want to convey my gratitude to my Summer Research supervisor and Teacher, Prof. Shantanu Rastogi for showing the research direction and for his valuable guidance, encouragement and support during my Summer Research. I express special thanks to Dr. Prabhunath Prasad who accompanied me in discussions. I am also thankful to Rahul bhaiya and Rashmi di for their guidelines.

I am especially thankful to Prayag bhaiya for his 24x7 company, guardianship and as a host for my stay.

The Science Academies summer research program needs special mention as this program not only gave me this opportunity to learn but also supported my stay financially.

(Bhaskar Anand)

Summary

The report summarizes my works as Summer Research Fellow at Department of Physics, DDU Gorakhpur University from 1st April, 2016 to 30th May, 2016. During the first four weeks from 1st to 29th April, 2016, I focused on the basics of Astronomy, Spectroscopy and Interstellar Medium (ISM). I studied about stellar distance measurements, stellar evolution, types of astrophysical objects, etc. There are more than 150 molecules already detected in the Inter stellar medium (ISM). I did some Literature Survey to understand the research in the area of Molecular Astrophysics and read especially about Cyanopolyyne molecules. Cyanopolyynes are linear molecules detected in the ISM by their rotational and vibrational spectra.

During the first phase, I also studied about Linux Operating System and installed SuSe linux. I also studied about GAMESS (General Atomic and Molecular Electronic Structure System), a quantum computation software that I used for obtaining molecular structure and spectra (vibrational) of Cyanopolyynes.

In the final four weeks I obtained vibrational spectra of eight Cyanopolyynes using GAMESS. With the help of graphical visualization program JMOL the nature of different vibrations were studied. Origin software was used for Graphical representation. It is recognized that the Cyanopolyynes have mainly three important intense features that are due to C-H stretch, N≡C and C≡C stretches and C≡C-H bending vibrations. The variations in intensity and frequency of these modes with chain length is studied and discussed.

Detailed Report

Introduction:-

The interstellar medium (ISM) is the matter which exists in the space between the star systems in a galaxy. Generally people imagine that outer space is a complete vacuum, devoid of any material. Although the interstellar regions are more devoid of matter than any vacuum that can artificially be created on earth, there is significant matter in space. The ISM has very low densities and consists mainly of gas (99%) and dust. In total, approximately 15% of the visible matter in the Milky Way is composed of interstellar gas and dust. The ISM includes gas in ionic, atomic, and molecular form, as well as dust and cosmic rays. It fills interstellar space and blends smoothly into the surrounding intergalactic space. The ISM is primarily hydrogen followed by helium with trace amounts of carbon, oxygen, and nitrogen [1].

The ISM is considered to have multiple phases depending on the medium density and temperature. These phases are also closely related to the proximity of stars in the region. The ISM dust and gas play very crucial role in the formation of new stars. More than 150 molecules have been detected in the ISM and circumstellar envelopes of stars shedding their outer envelopes [2]. Among the possible molecules, very big cyclic molecules e.g. polycyclic aromatic hydrocarbons (PAHs) are also observed in a variety of objects [3]. In the present work we have focused on Cyanopolyynes, these are linear molecules detected in the ISM by their rotational and vibrational spectra.

Cyanopolyynes:-

Cyanopolyynes are a group of linear molecules with the chemical formula HCnN (n=3, 5, 7, …). Structurally, they are polyynes with a Cyano group covalently bonded to one of the terminal acetylene units. A rarely seen group of molecules both due to the difficulty in production and the unstable nature of the paired groups, the Cyanopolyynes have been observed as a major organic component in interstellar clouds [4]. Cyanoacetylene (HC3N) was first discovered in interstellar molecular clouds in 1971 using millimeter wave and microwave telescopes [4]. Since then many higher Cyanopolyynes such as HC5N, HC7N and HC11N have also been discovered. Still higher Cyanopolyynes are expected in the ISM but their identifications are yet disputed. Other derivatives such as methyl-cyanoacetylene (CH3C3N) and ethyl-cyanoacetylene (CH3CH2C3N) have also been observationally detected [5].

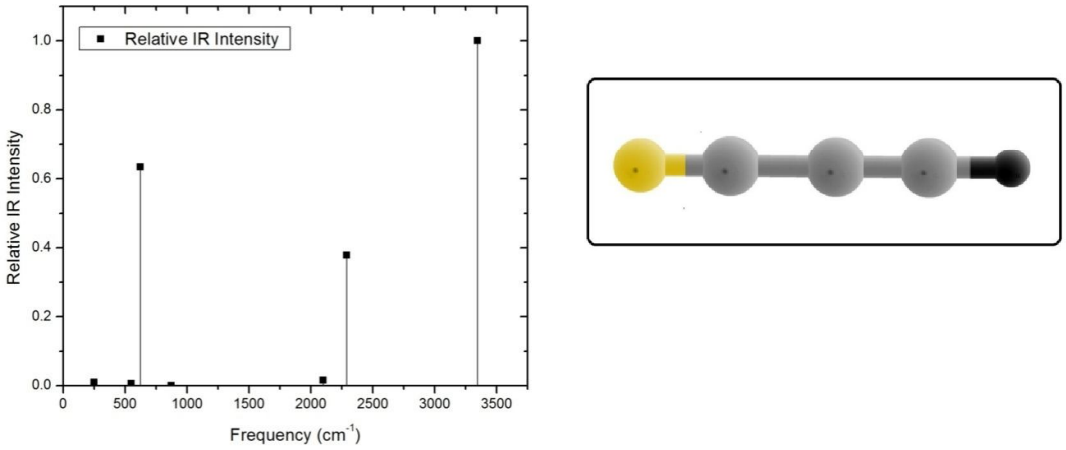
Using quantum chemical methods via GAMESS software study of eight Cyanopolyynes is performed. The equilibrium linear structures of Cyano-acetylene to Cyano-octaacetylene are obtained and their vibrational frequencies and infrared intensities are calculated. The results of each molecule are presented below.

01. Cyanoacetylene:

Cyanoacetylene is the simplest example of Cyanopolyynes, H−C≡C−C≡N. It is common on earth and is believed to be the initial reagent for the photo-catalyzed formation of higher interstellar Cyanopolyynes. Cyanoacetylene is one of the molecules that was produced in the Miller–Urey experiment and is expected to be found in carbon-rich environments [6]. It was first detected in 1971 in Sgr B2 via a rotational band and confirmed through several observations that include the detection of other rotational lines [7, 8]. Two of the ^{13}C isotopomers are also reported [9]. In the extragalatic regions it was first reported in 1990 toward the Silver Dollar galaxy. HC3N was also observed in comet Hale-Bopp by Bockelée-Movan et al. [10] and in Titan's atmosphere by Kunde et al. [11], making it one of the most diversely observed astromolecules to date.

01.Cyanoacetylene

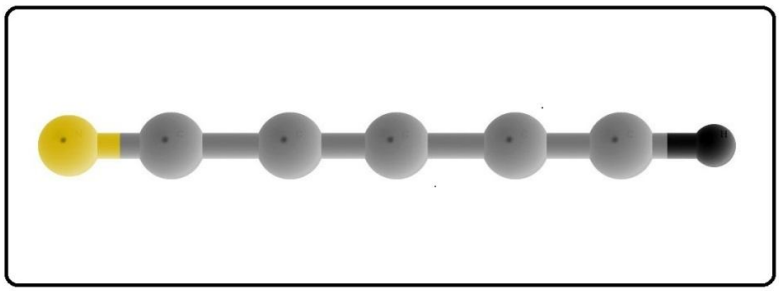
Frequency cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
650.55	624.528	1.14037	0.633722
650.56	624.5376	1.14037	0.633722
910.18	873.7728	0.00001	5.56E-06
2185.68	2098.253	0.02755	0.01531
2383.96	2288.602	0.68057	0.378204
3487.06	3347.578	1.79948	1



01. Vibrational Spectra of Cyanoacetylene

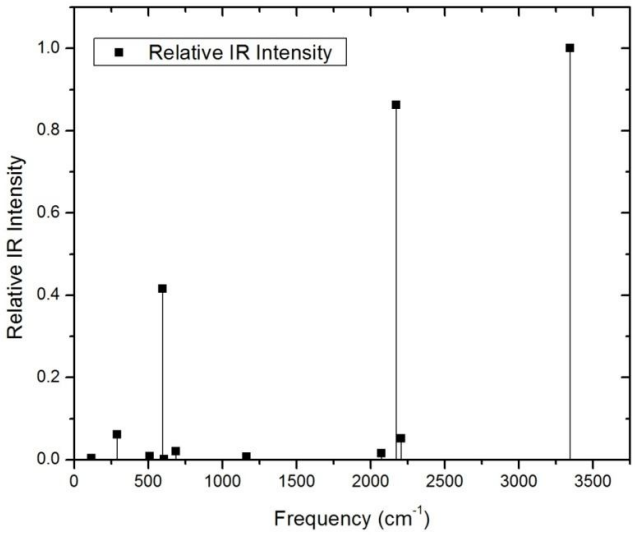
02. Cyanodiacetylene:

The detection of cyanodiacetylene (HC5N) through observations of multiple rotational transitions was spread through a number of reports across the span of several years in a variety of interstellar objects. Avery et al., 1976 [12] first reported the 4-3 line in Sgr B2 using the 46 m telescope at Algonquin Radio Observatory in Canada. Two more lines, 1-0 and 8-7, were reported later in the same year by Broten et al. [13], also in Sgr B2 using the observational facility in Parkes, Australia. Little et al., 1977 [14] reported observing the 9-8 line in the Heiles2 dust cloud. The same line was subsequently observed by Winnewisser & Walmsley in IRC +10216 in 1978 [15]. A fifth line, for the 2-1 transition, was found in Sgr B2 and Taurus Molecular Cloud -1 (TMC-1) by Gardner & Winnewisser, 1978 [16]. The 3-2 transition was observed by Rodriguez & Chaisson, 1980 [17], while Jennings & Fox observed four consecutive transitions (7-6, 8-7, 9-8, 10-9) in 1982 [18].



02. Cyanodiacetylene

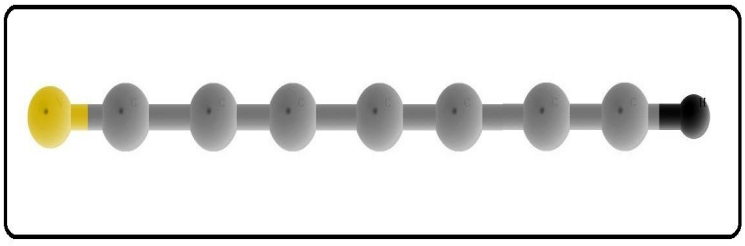
Frequency Cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
304.26	292.0896	0.15749	0.06059
304.26	292.0896	0.1575	0.060594
620.87	596.0352	1.08123	0.415976
620.88	596.0448	1.08124	0.41598
717.38	688.6848	0.05169	0.019886
717.39	688.6944	0.05171	0.019894
2158.03	2071.709	0.03998	0.015381
2296.74	2204.87	0.13229	0.050895
2263.45	2172.912	2.24287	0.862888
3486.46	3347.002	2.59926	1



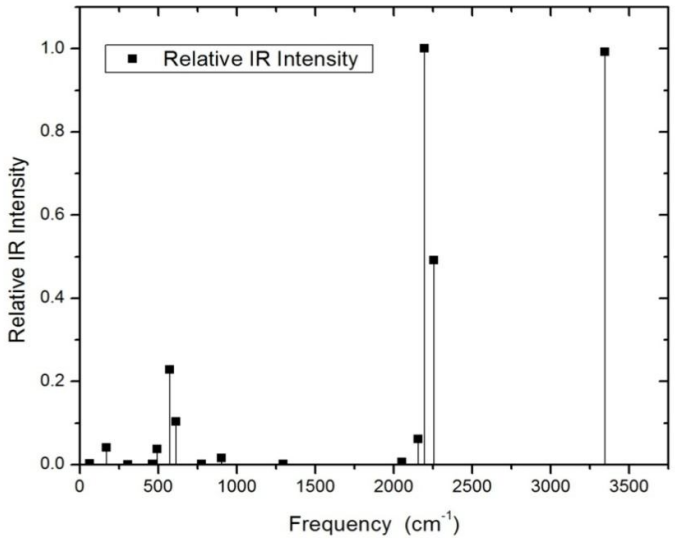
02. Vibrational Spectra of Cyanodiacetylene

03. Cyanotriacetylene:

Cyanotriacetylene or cyanohextriyne (HC7N) was initially detected by Kroto et al., 1978 [19] toward Heiles 2 (TMC-1). The observations were performed with the 46m telescope at the Algonquin Radio Observatory in Ontario, Canada. The initial detection was quickly confirmed by Little et al. [20], who observed HC7N in TMC-2, and by Winnewisser & Walmsley [15], who observed it in IRC+10216. Subsequent observations by Gardner et al. [21], Rodriguez & Chaisson [17], Snell et al. [22], and Cernicharo et al. [23] extended the number of observed lines of HC7N and added new sources, including Sgr B2 and Ll544.

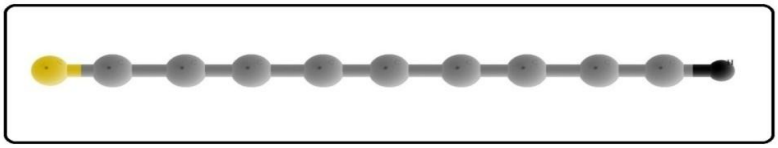


03. Cyanotriacetylene			
Frequency cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
178.53	171.3888	0.1383	0.040769761
178.53	171.3888	0.1383	0.040769761
515.94	495.3024	0.12718	0.037491672
515.94	495.3024	0.12721	0.037500516
597.96	574.0416	0.77858	0.229519312
597.97	574.0512	0.77842	0.229472145
639.51	613.9296	0.35261	0.103946678
639.51	613.9296	0.35283	0.104011532
942.17	904.4832	0.05187	0.015290871
2248.09	2158.166	0.20961	0.061791393
2288.55	2197.008	3.41795	1.007585003
2350.38	2256.365	1.67669	0.494275135
3486.51	3347.05	3.39222	1

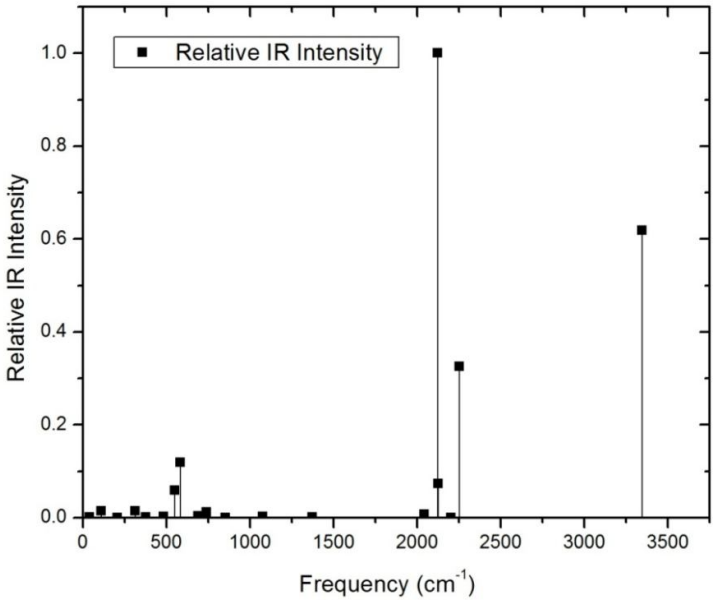


02. Vibrational Spectra of Cyanotriacetylene

04. Cyanotetraacetylene:

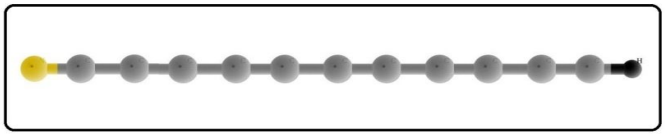


04. Cyanotetraacetylene			
Frequency cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
115.86	111.2256	0.09417	0.013928
115.86	111.2256	0.09417	0.013928
325.82	312.7872	0.09695	0.014339
325.82	312.7872	0.09694	0.014337
573.75	550.8	0.3924	0.058036
573.75	550.8	0.39231	0.058023
607.02	582.7392	0.80163	0.118561
607.02	582.7392	0.80172	0.118574
769.92	739.1232	0.08028	0.011873
2213.51	2124.97	0.49431	0.073108
2235.23	2145.821	6.76133	1
2345.35	2251.536	2.20089	0.325511
3486.4	3346.944	4.18422	0.618846

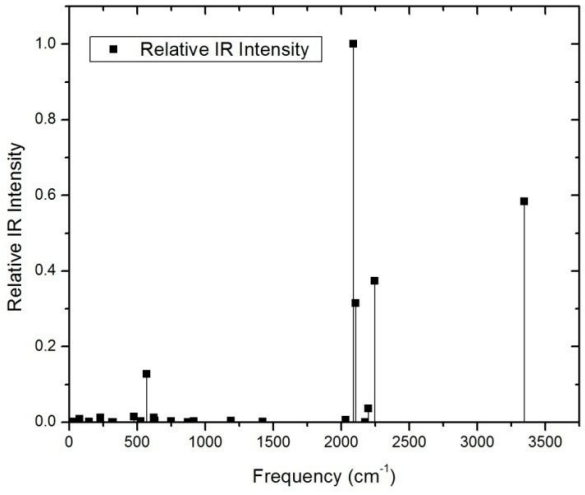


04. Vibrational Spectra of Cyanotetraacetylene

05. Cyanopentaacetylene:

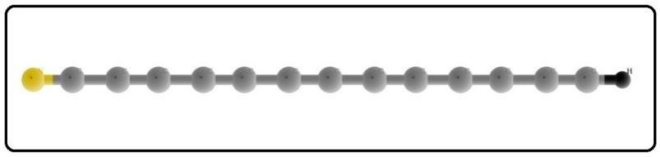


05. Cyanopentaacetylene			
Frequency cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
241.75	232.08	0.10071	0.011665
496.08	476.2368	0.11683	0.013533
496.08	476.2368	0.11686	0.013536
595.87	572.0352	1.09645	0.127005
595.88	572.0448	1.09652	0.127013
650.31	624.2976	0.10266	0.011891
2178.24	2091.11	8.63315	1
2193.65	2105.904	2.71638	0.314645
2292.6	2200.896	0.30952	0.035852
2340.99	2247.35	3.22662	0.373748
3486.78	3347.309	5.03481	0.583195

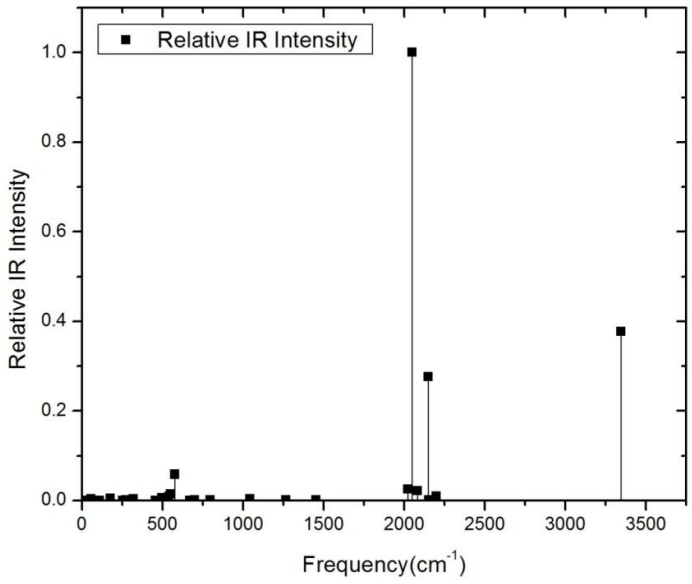


05. Vibrational Spectra of Cyanopentaacetylene

06. Cyanohexaacetylene:

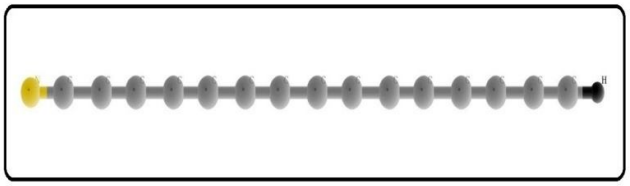


06. Cyanohexaacetylene			
Frequency cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
575.22	552.2112	0.22575	0.014595827
575.24	552.2304	0.2254	0.014573197
601.72	577.6512	0.89533	0.057887404
601.77	577.6992	0.89784	0.058049687
2108.15	2023.824	0.39146	0.025309777
2136.89	2051.414	15.46675	1
2171.31	2084.458	0.32217	0.020829845
2239.51	2149.93	4.26497	0.275750885
3484.88	3345.485	5.82322	0.376499265

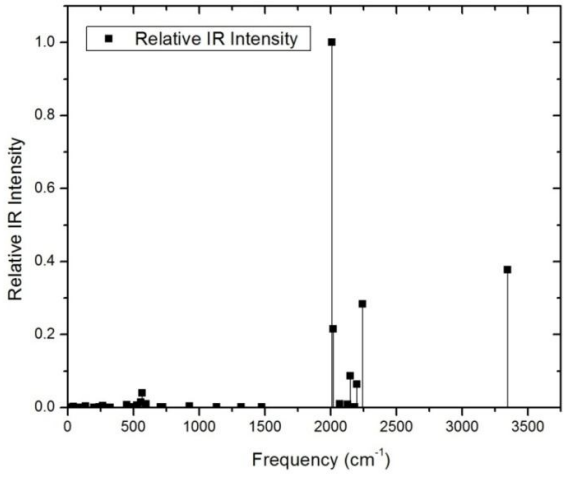


06. Vibrational Spectra of Cyanohexaacetylene

07. Cyanoheptaacetylene:

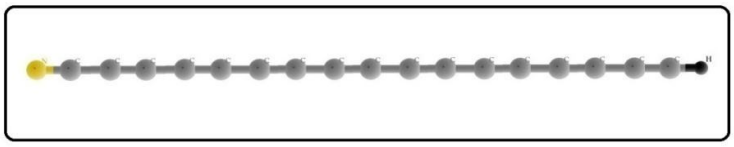


07. Cyanoheptaacetylene			
Frequency cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
581.17	557.9232	0.2536	0.01438409
581.17	557.9232	0.25394	0.014403375
592.18	568.4928	0.69542	0.039443944
592.18	568.4928	0.69573	0.039461527
2095.21	2011.402	17.63059	1
2103.06	2018.938	3.79706	0.215367722
2239.57	2149.987	1.52612	0.086560915
2291.12	2199.475	1.11386	0.063177693
2338.13	2244.605	4.99759	0.283461302
3487.1	3347.616	6.64168	0.376713428

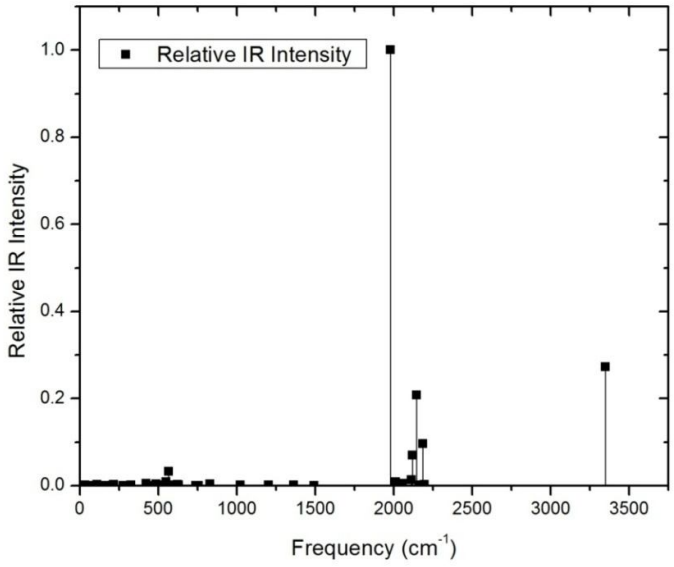


07. Vibrational Spectra of Cyanoheptaacetylene

08. Cyanooctaacetylene:



08. Cyanooctaacetylene			
Frequency cm^{-1}	**Frequency*** cm^{-1}	**IR Intensity** $Debye^2/Amu\ Å^2$	**Relative Intensity**
592.04	568.3584	0.86999	0.031902
592.05	568.368	0.87019	0.031909
2061.85	1979.376	27.27082	1
2095.92	2012.083	0.22519	0.008258
2143.92	2058.163	0.1142	0.004188
2199.82	2111.827	0.34693	0.012722
2209.34	2120.966	1.89114	0.069347
2276.9	2185.824	2.61999	0.096073
2337.62	2244.115	5.66276	0.207649
3487.17	3347.683	7.43418	0.272606

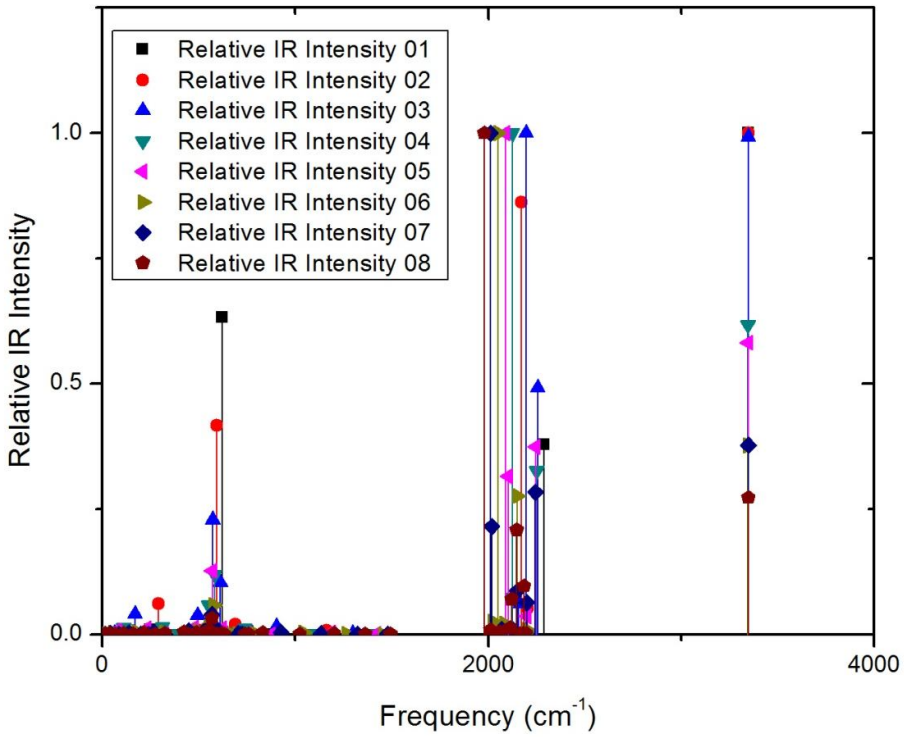


08. Vibrational Spectra of Cyanooctaacetylene

Discussions:-

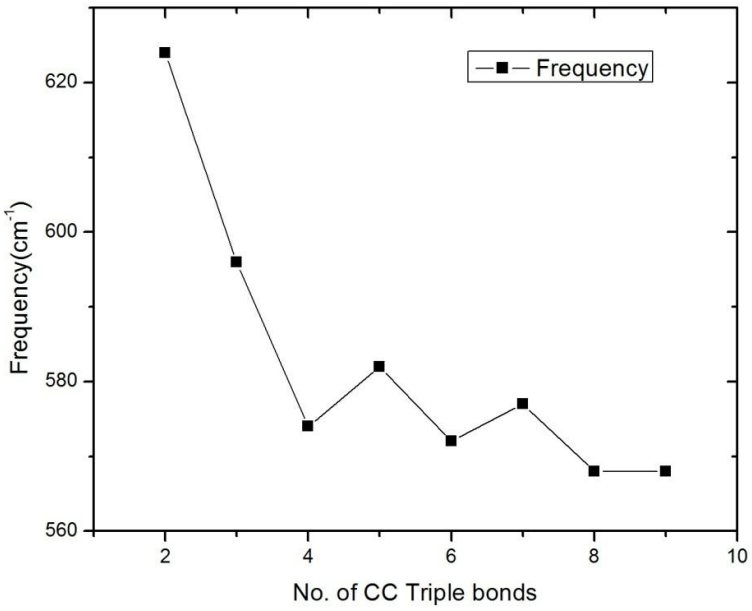
Although Cyanopolyynes higher than Cyanotriacetylene have not yet been confirmed in the ISM, we have studied their vibrational spectra. In all the molecules there are mainly three important intense features, which are due to C-H stretch, N≡C and C≡C stretches and C≡C-H bending vibrations. A combined spectra of all the molecules is plotted in figure 09. The observed frequency due to C-H stretch is sharp and it is at 3347 cm^{-1}. This mode is independent of the length of the molecule and appears at the same frequency in all Cyanopolyynes.

The second mode lies in the 2290 to 2148 cm^{-1} region. These modes are primarily due to N≡C and C≡C stretch vibrations. The intensity of this feature increases with the length of the chain. The frequency due to C≡C-H bending vibration is nearly constant at around 600 cm^{-1}.



09. Combined Vibrational Spectra of Cyanopolyynes

It is interesting to study the variations in frequency of modes due to C≡C-H bending with number of C≡C bonds (triple bonds) in the molecule. Figure 10 shows this variation. As the chain length increases initially the frequency decreases. Beyond Cyanotriacetylene there is frequency alternation. The frequency is lower for even number of C≡C and is higher for odd number of C≡C. This alternation dampens and for very large chain the frequency of this mode becomes constant at 568 cm^{-1}.



10. Variation of Frequency with increasing no. of

Triple bonded carbon for C≡C-H bending

It may be noted that in all quantum chemical calculations the vibrational frequencies are over estimated. In order to bring them close to the actual observed spectral frequencies scaling is required. The scaling procedures can be complicated for large molecules and be frequency dependent [24]. But in these relatively small molecules we have taken a frequency independent scaling factor of 0.96. This value is arrived at by comparing the reported spectra of Cyanoacetylene and by considering the values used in other complex molecules [24].

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